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CONTENTS

1 **Organic Sulphur Compounds in Alberta Cracked Distillates**
By C. H. Amberg

9 **Some Observations Concerning the Viscosity–Temperature Behaviour of Hydrocarbons**
By W. C. Winning

16 **Studies in Shale Oil. Part IX. Further Data on Emulsions and Sludges**
By Geo. E. Mapstone

Abstracts 1–103

Book Reviews

Additions to the Library

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ORGANIC SULPHUR COMPOUNDS IN ALBERTA CRACKED DISTILLATES *

By C. H. AMBERG †

SUMMARY

A comparatively rapid method has been developed for the identification of sulphur compounds in high-sulphur cracked distillates. The fractionated samples were chromatographed by displacement from an alumina column. Liquid cuts were thus obtained that were enriched with respect to organic sulphur compounds. These in turn were subjected to analysis by a combination of gas–liquid partition chromatography and mass spectrometry.

The method was employed for the examination of cuts from a thermally and a catalytically cracked distillate of Lloydminster crude boiling up to the xylene range and from a thermally cracked distillate of Alberta bitumen boiling up to 166° C. It appeared that all the sulphur compounds existing in high enough concentration to make individual identification possible by this method were thiophenic in nature. A semi-quantitative estimate of 15 different thiophenes was obtained.

INTRODUCTION

THERE is an increasing need for the study of organic sulphur compounds in petroleum in view of the growing use of crude oils of high sulphur content. Several papers have appeared on the subject, notably those of API Project 48 [1, 2], but relatively little has been reported specifically on Canadian oils.[3, 4] Moreover, the bulk of the work done has dealt with crudes, because cracked distillates usually present additional problems that have not been altogether satisfactorily solved.

In the present work an attempt has been made to identify organic sulphur compounds in cracked distillate fractions from Alberta oils up to the boiling range of the C_9 aromatics. This was done by employing a combination of chromatographic techniques and mass spectral analysis in the case of the predominantly occurring thiophenes. In a previous publication from this laboratory, Peterson, Keller, and Gishler [5] reported the probable occurrence of thiophene and the methylthiophenes in Alberta distillate fractions.

SEPARATION OF KNOWN ORGANIC SULPHUR COMPOUNDS BY CHROMATOGRAPHY

Distillates in the gasoline boiling range may be separated by chromatography to varying degrees of completion. For instance, the Fluorescent Indicator Adsorption Method [6] tentatively adopted by the ASTM [7] employs a specific activated silica gel to separate quantitatively paraffins, olefins, and aromatics in that order. Sulphur compounds (as well as other polar compounds) tend to accumulate near the end of the aromatic region, but can be displaced by appropriate alcohols.

Thompson and co-workers [1] found that Alcoa alumina type H–41 gave good separations of sulphur compounds from aromatics. They used elution chromatography followed by displacement of the residual compounds with ethyl alcohol. In the experiments described here it was found expedient to use displacement techniques only. This has the advantage that the fractions collected from the chromatographic column are in the pure form, and thus need not be separated from eluents. At the same time sufficiently high concentrations of sulphur compounds can be obtained in a single-stage separation to render profitable further analysis of the high-sulphur fractions.

(1) *Apparatus and Methods*

Alcoa type H–51 activated alumina was selected after a number of trials with different silica and alumina gels. This is very similar in both physical properties and chemical composition to type H–41, which is no longer available. The gel was pre-treated by floating off fines that remained suspended after 7 minutes in a beaker of water approximately 20 cm high.[8] This procedure was repeated twice. Before use the gel was dried for 4 hours at 200° C.

Two glass columns were used. One of these was 2 m long and consisted of three main sections of 16, 13, and 7 mm i.d. with a short 7-mm constriction between the first two sections.[6] This column held 270 g of the dry gel. The sample to gel ratio used was generally of the order of 1 : 10 by weight. *iso*Propyl alcohol was employed as the displacing agent; nitrogen pressures were adjusted so that a total run would last approximately 20 hours, sample fractions being collected at the rate of 5–8 ml/hr. Each fraction was characterized by refractive index measurements.

The second column measured 1 m in length and 6 mm in diameter apart from a short and somewhat wider section at the top, followed by a constriction. This column, which held 26 g of dry alumina, was used chiefly in gel regeneration experiments.

(2) *Gel Regeneration*

In order to test the performance of the activated alumina in terms of the benzene–thiophene separation after repeated regeneration, a batch of gel was taken

* MS received 8 August 1958. Issued as N.R.C. Publication No. 4984
† Div. of Applied Chemistry, National Research Council, Ottawa, Canada.

through a series of cycles involving slurrying with benzene, washing, filtering, and drying. It can be seen from Fig 1 that there was no significant change in gel performance through 19 cycles.

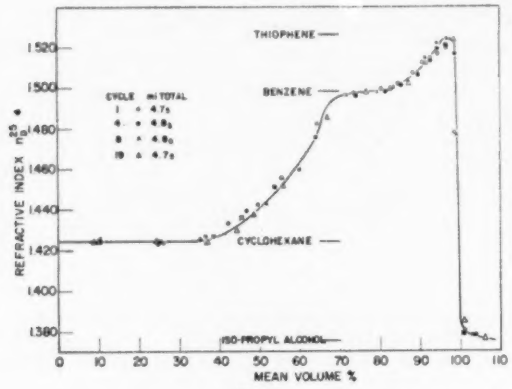

FIG 1

REGENERATION OF ACTIVATED ALUMINA GEL

(3) *Results and Discussion*

Preliminary runs were made with known compounds in order to test the ability of the activated alumina to separate aromatics from sulphur compounds. Furthermore, material losses with respect to total liquid and with respect to sulphur compound were evaluated in separate runs.

The assessment of the sulphur content of the various fractions collected was made on the basis of refractive index measurements and gas–liquid partition chromatography (GLPC).[9]

Fig 2 shows the benzene–thiophene separation in a sample containing 34·2 per cent benzene and 12·0 per cent thiophene, along with *cyclo*hexane and hexene-1 (30·2 and 23·6 per cent respectively). Approximately 97 per cent of the benzene and thiophene was recovered. The *cyclo*hexane and hexene-1 separation is not shown, as no particular care was taken with the recovery of these substances. Separations of the paraffin–olefin type are much sharper on appropriate silica gels.[10]

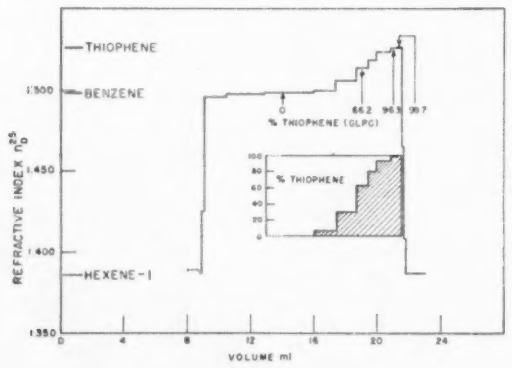

FIG 2

BENZENE–THIOPHENE SEPARATION ON ALUMINA GEL

The separation of benzene and diethyl sulphide is shown in a similar manner in Fig 3. The original mixture contained 25·9 per cent *cyclo*hexane, 29·8 per cent hexene-1, 33·7 per cent benzene, and 10·6 per cent diethyl sulphide. The complete adsorptogram for a mixture of *cyclo*hexane, benzene, and *n*-amyl mercaptan (48·5, 40·7, and 10·8 per cent respectively) is shown in Fig 4.

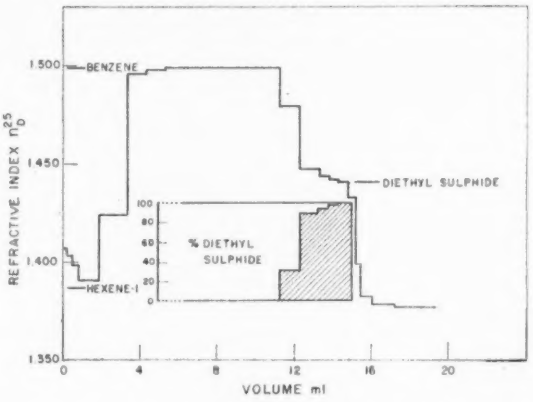

FIG 3

BENZENE–DIETHYL SULPHIDE SEPARATION ON ALUMINA GEL

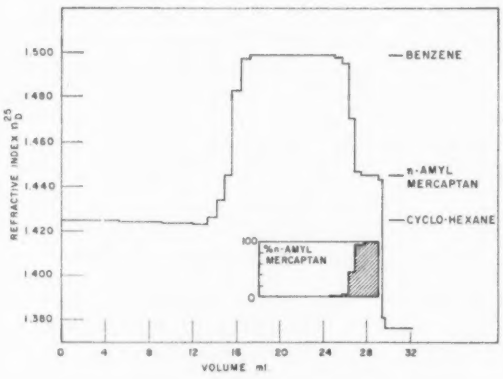

FIG 4

BENZENE–*n*-AMYL MERCAPTAN SEPARATION ON ALUMINA GEL

A comparison of the behaviour of the three sulphur compounds is given in Fig 5. It should be noted that the origin in this graph coincides with the boundary between the sample and the displacing alcohol, *i.e.* the curves read downward along the chromatographic column. The relative adsorbability

of the compounds appeared to be in line with earlier work done on silica gel.[11]

Because of the small size of many of the fractions collected, it was not possible to perform the necessary analyses and also study the recovery of both total liquid and sulphur compounds. For this reason a number of runs was done without fractionation.

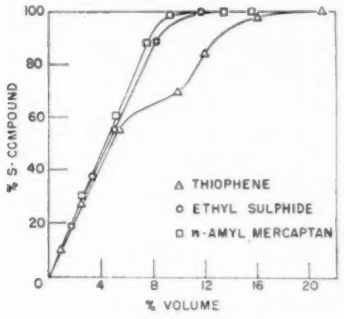

FIG 5

CHROMATOGRAPHIC SEPARATION OF SULPHUR COMPOUNDS ON ALUMINA GEL

Each sample was weighed and analysed for total sulphur content by the bomb method before and after a run. Representative results are shown in Table I.

In summary it may be stated that the expected loss, both with respect to total liquid and with respect to sulphur alone, is not likely to exceed 4 per cent, but is on the average about half that amount, up to the alcohol boundary. Moreover, sulphur compounds that overlap into the alcohol region can usually be analysed by GLPC; they may be recovered, if necessary.[1]

ANALYSIS OF DISTILLATE FRACTIONS

Peterson, Keller, and Gishler [5] have reported the results from the fluidized solids coking of a number of Canadian high-sulphur crudes using both a sand bed and a silica–alumina catalyst bed. A number of fractionated samples from this work had been stored under refrigeration and were still available. The two series chosen from these for the present investigation were thermally and catalytically cracked distillates derived from a crude from the Lloydminster field 150 miles E. of Edmonton. The cracking temperatures were 515° and 475° C, respectively. Both these had been closely fractionated; they were roughly 2½ years old. Pertinent data characterizing the fractions are reproduced in Table II.

A third series of samples was derived from the thermal cracking at 600° C of hot-water separated Fitzsimmons crude (Alberta bituminous sands). The details of the pilot plant run will be reported elsewhere by W. S. Peterson. The decanted light oil from this run was fractionated in a 25 mm × 36 inch Podbielniak Hyper-Cal high temperature adiabatic distillation column as described previously.[5] Chromatographic separations were all completed within 10 weeks of fractionation, although some of the final group analyses were done as much as 18 weeks later.

Table III shows the fractionation data and hydrocarbon type analyses done on the fresh gasoline fractions by the FIA method,[6] as well as the total percentage of sulphur.

TABLE I

Chromatography on H–51 Alumina Gel—Material Balance

Run	Sulphur compound	*cyclo*-Hexane %	Benzene %	*S*-compound %	Sample weight g	Liquid loss %	Sulphur %	Sulphur loss %
23	Thiophene	49·1	38	12·9	19·22	1·9	4·91	3·3
24 *	Thiophene	46·6	38·5	14·9	22·55	3·5	5·79	1·4
25	Diethyl sulphide	47·4	38·6	14·1	19·2	1·4	5·07	2·6
26	Diethyl sulphide	52·5	36·9	10·6	20·88	1·4	3·85	2·6
30	*n*-Amyl mercaptan	52·9	35·2	11·8	16·45	1·8	3·38	1·5
31	*n*-Amyl mercaptan	51·8	38·5	9·9	17·63	2·6	2·64	2·3

* Using *iso*amyl alcohol instead of *iso*propyl alcohol.

TABLE II

Catalytically (M) *and Thermally Cracked* (P) *Lloydminster Crude. Fractionation and Analyses (from Peterson, Keller, and Gishler)*

Fraction No.	% Dist.	B.p., °C	Hydrocarbon types			% S (present data)
			% Sat.	% Ol.	% Ar.	
M–1	23·3	66	14·2	84·8	1	0·05$_6$
2	27·3	68	9·4	88·2	2·4	0·05$_6$
3	37·7	90	17·6	65·7	16·7	0·35
4	44·5	99	23·5	73·1	3·4	0·05$_6$
5	55·8	118	18·9	42·8	38·3	1·11
6	60·6	129	26·8	67·1	6·1	0·22
7	69	140	19·4	24·8	55·8	0·98
8	71·1	145	13·5	32·1	54·4	1·1
P–1	16·7	69	5·2	92·9	1·9	0·21
2	23·9	87	6·9	67·7	25·4	0·78
3	31	97	16·2	79·5	4·3	0·06$_6$
4	44·5	118	17·6	54·7	27·7	1·18
5	50·6	127½	21	73·7	5·3	0·26
6	62·6	145	18·4	49·6	32	1·26

(1) *Benzene and Toluene Fractions*

Fractions boiling in the benzene range (M–3, P–2, R–2) and in the toluene range (M–5, P–4, R–4) in each

of the three series of distillates were chromatographed on the alumina column as described, and the appropriate eluates were further analysed on a GLPC column. The thiophenes in the two boiling ranges were easily separated. As an example, Fig 6 shows

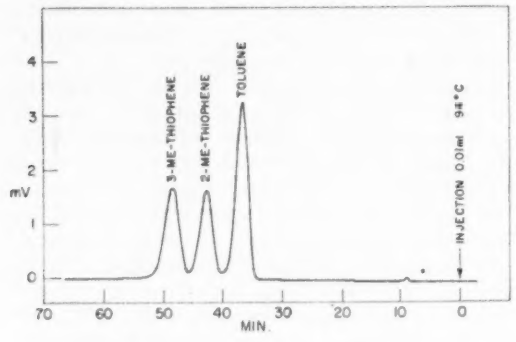

FIG 6

GLPC ANALYSIS OF HIGH-SULPHUR FRACTION FROM M–5

the separation of toluene, 2-methylthiophene, and 3-methylthiophene in a high-sulphur concentrate from M–5 by GLPC on a 12-foot column at 94° C.

TABLE III

Thermally Cracked Alberta Bitumen. Fractionation and Analyses

Fraction No.	% Dist.	B.p., °C	Hydrocarbon types			% S
			% Sat	% Ol.	% Ar.	
R–1	2·2	68	3·5	94·8	1·7	0·19
2	10·8	88	1·5	13·8	84·7	1·28
3	12·6	104	7·1	68·1	24·8	1·02
4	32	118	0·8	7·9	91·3	1·99
5	33·4	129	10	82	8	1·62
6	49·2	140½	2·6	9·1	88·3	2·41
7	57·1	146½	3·4	13·3	83·3	2·42
8	60·3	158	15	27·3	57·7	2·45
9	69·6	166	6·1	12·1	81·8	4·94
10	74·2	170	7·9	9·7	82·4	2·16
11	78·7	175½	13·5	13·1	73·4	1·88
12	84·6	181½	9·9	9	81·1	3·1
13	88·2	186½	11·3	9·5	79·2	3·75
14	93·7	190½	15·5	12·7	71·8	2·64
15	96·8	195	13·1	8·2	78·7	2·98
16	100	200	13·7	9·4	76·9	2·09

The eluent gas was nitrogen, and the stationary phase tricresyl phosphate supported on C–22 firebrick, 35–80 mesh.[9]

The identity of the peaks was confirmed by comparing their elution times relative to a standard with the known compounds. Furthermore, mass spectrometric analysis of the high-sulphur concentrates showed the presence of thiophene in the benzene fractions and of methylthiophene in the toluene fractions, without distinguishing clearly the two isomers in the latter instance.

In no case were other types of sulphur compounds detected by these methods. It is difficult to assign limits of detectability, since they vary with individual mixtures. The mass spectrometer used, a 90° magnetic-sector-type instrument, will detect substances down to a concentration of roughly 0·1 per cent in very favourable cases. If overlapping of one or more of the chief mass-to-charge ratio peaks takes place, the lowest limit might well be of the order of 5 per cent before the presence of a lesser component could be detected in unknown mixtures.

TABLE IV

Thiophenes in Benzene and Toluene Fractions

Fraction	% S Total	% S Thiophenes
M–3 . . .	0·35	0·37
M–5 . . .	1·11	1·3
P–4 . . .	1·18	1·1
R–2 . . .	1·28	1·3
R–4 . . .	1·99	2·09

In a similar fashion 0·1 per cent can be regarded as a working lower limit of detectability for the GLPC apparatus used, if the elution peaks are well separated and depending also on peak sharpness. By retaining separate cuts from the GLPC separation in a cold trap and subjecting them to mass spectrometric analysis it was possible within the above 5 per cent limit to check on sulphur compounds that might have been missed due to overlap in the GLPC peaks.

An additional measure of the probable maximum amount of unidentified sulphur compounds was gained by comparing the total percentage of sulphur in a fraction to the percentage of thiophenic sulphur recovered. Because of the many experimental steps

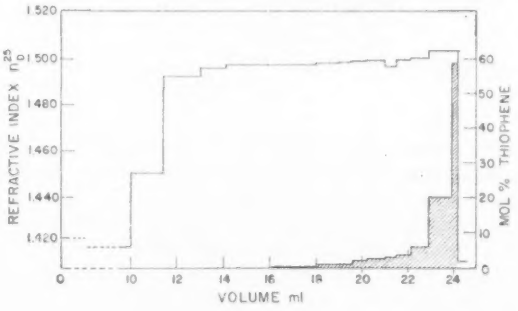

FIG 7

CHROMATOGRAPHIC ANALYSIS OF BENZENE FRACTION R–2, ALBERTA BITUMEN

involved, this comparison was not expected to be better than ±5 per cent with fresh distillates (R-distillation); with samples after extended storage this became roughly ±10 per cent. In the latter case oxidized and probably polymerized products tended to interfere with the GLPC analysis.

Table IV shows the results of such a comparison. Here column 2 gives the total percentage of sulphur

in the distillate fraction and column 3 the percentage of sulphur as thiophenes calculated from the GLPC analyses of all subsequent cuts from the alumina column. The chromatograms and composition of fractions R–2 and R–4 are presented as detailed examples in Figs 7 and 8. It can be seen from the table that no other major component containing

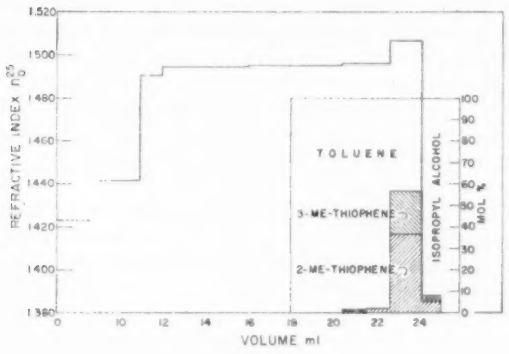

FIG 8

CHROMATOGRAPHIC ANALYSIS OF TOLUENE FRACTION R–4, ALBERTA BITUMEN

sulphur was likely to be present in the benzene and toluene fractions. Further confirmation became evident from the sulphur group analyses (v.i.). The tendency for the thiophenic sulphur to be somewhat higher than the total sulphur would suggest a systematic error, but more data are required before this can be definitely established.

(2) *Fractions in the Xylene and C_9 Aromatics Boiling Range—Analysis by Mass Spectrometer*

Fractions P–6, M–7, M–8, and R–6 to R–9, whose properties are shown in Tables II and III, were treated in the same way as the benzene and toluene fractions previously discussed.

In order to achieve a relatively rapid, semi-quantitative identification of the sulphur compounds present, it was decided to limit the pre-concentrating stage to a single-pass chromatographic separation by displacement from the H–51 alumina column. The high-sulphur fraction thus obtained might still contain a considerable amount of aromatic hydrocarbons, but the two types of compounds can be readily differentiated on the mass spectrometer. Paraffins and olefins were completely removed, but styrene homologs invariably appeared together with the alkylthiophenes near the alcoholic boundary on the alumina column.

As previously shown,[9] the six C_6 thiophenes can be separated by GLPC on a tricresyl phosphate column with relative ease. There occurred, however, a certain amount of overlap with aromatics. With the aid of Fig 9 one may visualize the relative position of peaks on the chromatogram. Here the logarithm of the relative elution time of the compounds at the conditions indicated was plotted against the number of carbon atoms in the molecule.[12] Inspection of the points representing dimethyl- and ethyl-isomers in Fig 9 suggests a natural division into three groups, which, indeed, was followed for trapping out the GLPC eluates and subsequent mass spectrometric analysis.

In order to analyse the spectra obtained, use was made of the method of mass spectral correlations described by Kinney and Cook [13] and applied by Kinney, Smith, and Ball to the identification of thiophenes in

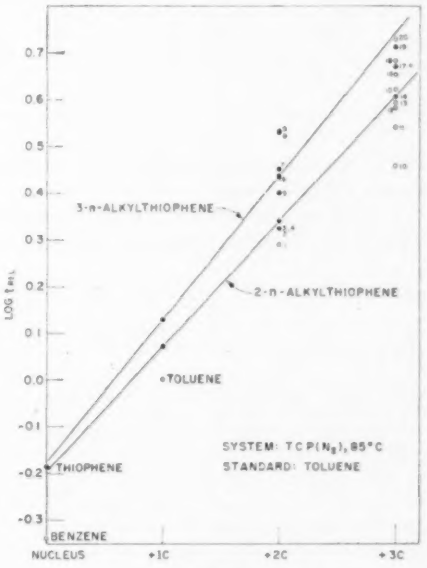

FIG 9

RELATIVE ELUTION TIMES OF ALKYLTHIOPHENES AND AROMATIC HYDROCARBONS

●: Thiophenes (*n*-alkylthiophenes not numbered)
○: aromatic hydrocarbons

1. Ethylbenzene
2. 2,5-Dimethylthiophene
3. *p*-Xylene
4. *m*-Xylene
5. 2,4-Dimethylthiophene
6. *o*-Xylene
7. 2,3-Dimethylthiophene
8. Styrene
9. 3,4-Dimethylthiophene *
10. Cumene
11. *n*-Propylbenzene
12. *p*-Ethyltoluene
13. *m*-Ethyltoluene
14. 2-Methyl-5-ethylthiophene *
15. Allylbenzene *
16. Mesitylene
17. 2,3,4-Trimethylthiophene (tentative) *
18. *o*-Ethyltoluene
19. 2,3,5-Trimethylthiophene *
20. 1,2,4-Trimethylbenzene (tentative) *

* Not confirmed with known compound.

shale-oil naphtha.[14] In instances where no spectra and sensitivities had been published in the API catalogue,[15] recourse was taken to values given in the above publications and by Hartough.[16] Our own spectra were determined where possible. Examples of characteristic peaks for 3-ethylthiophene and

2,3-dimethylthiophene are given in Table V. The 3-ethylthiophene was an API sample of over 98 per cent purity [17] and the 2,3-dimethylthiophene was obtained by chromatographing a commercially impure sample on a GLPC column.

TABLE V

Comparison of Mass Spectra. Relative Ion Intensities

Ion	3-Ethylthiophene		2,3-Dimethylthiophene	
	Ref. [18]	Present data	API Serial No. 502	Present data
112^+	38·9	42·7	83·4	104
111^+	7·5	8·5	83·2	90
97^+	100	100	100	100
85^+	2·6	2·5	4·6	5·4
84^+	4	4·1	1·7	1·4
59^+	1·4	1·4	13·8	14·9
58^+	—	—	10·9	10·1

In the following the method of analysis is outlined by means of the R-series. Since the magnitudes obtained cannot be regarded as better than semi-quantitative, it has not been attempted to include in the analysis eluates from the alumina column that were collected ahead of the high-sulphur fraction.

The high-sulphur eluate of R–6 (129°–140½°) was separated by GLPC and trapped out in two cuts corresponding to the lower two groups of compounds of the xylene range in Fig 9. As expected from the boiling range, neither of the two compounds in the third group were present. They were, however, contained exclusively in R–7 (140½°–146½°). The relative ion intensities of four characteristic peaks measured for the two cuts in each case are shown in Table VI, together with those for the appropriate thiophene homologs.

On the basis of approximately equal sensitivities and using the 112^+ ion peaks the ratio of 2-ethyl to 2,5-dimethylthiophene in GLPC cut 1 of R–6 was estimated to be 2·4. This value was then used in a test for self-consistency to calculate the relative ion intensities of the 111 and 59 peaks, which worked out to be 57·4 and 11·9 respectively (observed, 61·4 and 11·8).

GLPC cut 2 was analysed in a similar fashion, only two peaks (112 and 111) had to be used to set up appropriate simultaneous equations for the three thiophenic constituents.

Analysis of fraction R–7 followed the same pattern as that of R–6, but was simplified in that only three thiophene homologs occurred. The higher boiling fractions R–8 (146½°–158°) and R–9 (158°–166°) were again subjected to the same treatment. Unfortunately in this boiling range only half the mass spectra of the possible thiophene isomers were known and, in fact, no physical data of any kind appeared to be available for 2-ethyl-4-methyl or for 3-ethyl-4-methylthiophene. 2-*tert*-Butylthiophene could have

TABLE VI

Relative Ion Intensities for R–6, R–7, and Alkylthiophenes

Ion	R–6		R–7		Alkylthiophenes					
	GLPC Cut 1	GLPC Cut 2	GLPC Cut 1	GLPC Cut 2	2-Ethyl	2,5-Dimethyl	3-Ethyl	2,4-Dimethyl	2,3-Dimethyl	3,4-Dimethyl
112^+	77·8	109	107	152	46	154	42·7	151	104	160
111^+	61·4	117	108	206	6·8	178	8·5	214	90	213
97^+	100	100	100	100	100	100	100	100	100	100
59^+	11·8	11·4	12·9	6·3	1·3	37·4	4·1	18	14·9	6

TABLE VII

Relative Ion Intensities for R–8, R–9, and Alkylthiophenes

Ion	R–8			R–9			
	GLPC Cut 3	2-Methyl-5-ethyl-thiophene	2-*n*-Propyl-thiophene	GLPC Cut 2	2,3,4-Tri-methyl-thiophene	GLPC Cut 3	2,3,5-Trimethyl thiophene
126^+	58	37	24·4	63	61	86	80
125^+	4·4	6	0·8	45	58	80	82
111^+	100	100	1·9	100	100	100	100
97^+	60	1·6	100	9	7	4·3	5·5
84^+	1·1	0·8	1·6	0·4	1	0	0·9
59^+	7·9	9·5	1·2	17	12	31	29

occurred in R–9, but no mass higher than 126 was detected by the mass spectrometer.

The relative ion intensities of such compounds as were identified with a fair degree of certainty are presented in Table VII together with those of the pure compounds from the above sources. Tentative estimates were made for the following thiophenes in R–8: GLPC cut 1 contained about 2 per cent of sulphur compounds which were mainly 2,3-dimethylthiophene and some 2-*iso*propylthiophene. The sulphur compounds in cut 2 were largely 3,4-dimethylthiophene along with some 3-*iso*propylthiophene, the latter being the only possible isomer of mass 126 to have eluted so early. Cut 3 contained a large amount of 2-methyl-5-ethylthiophene. Even though the mass spectrum alone did not uniquely establish the presence of this compound, some generalized concepts regarding the mass spectra of thiophenes,[13] as well as the consideration of boiling points and elution times, definitely favoured the 2,5-isomer. The high value for mass 97, Table VII, together with an elution time near that estimated from the lower straight line of Fig 9, suggested 2-*n*-propylthiophene as the other major constituent of mass 126 in GLPC cut 3.

The main thiophenic constituents of R–9 were identified with comparative ease. GLPC cut 1 extended over the same elution range as cut 3 in R–8 and contained the same compounds. The contents of the second and third GLPC cuts may be gathered from Table VII.

(3) *Summary of Thiophenes Identified*

The final estimates are summarized in Tables VIII and IX. Table VIII shows the percentage composition of the thiophenes in each of the fractions examined. In Table IX the results for fractions R–1 to R–9 are combined to give an estimate of the total amount in the gasoline cut of each of the thiophenes identified.

The following points may be noted: the sum total of the thiophenes boiling up to 166° accounts for at least 70 per cent of the total sulphur in the gasoline cut. This figure is a minimum, since the two trimethylthiophenes probably also occurred in the next higher fraction R–10. For the same reason also the apparent 1 : 1 ratio of the 2,3,4- and the 2,3,5-isomer cannot be regarded as significant. The comparative abundance of 2-methyl and 3-methylthiophene was in the ratio 2 : 1; for the analogous ethyl-isomers this became approximately 8 : 1, while their absolute abundance in terms of percentage of sulphur was only about one-third of that of the two methylthiophenes. This trend appeared to persist through the monosubstituted propylthiophenes. The single most abundant isomer detected was 2-methylthiophene.

TABLE VIII

Proportion of Alkylthiophenes in Fractions

Alkylthiophene	M–5	P–4	R–4	M–7	M–8	P–6	R–6	R–7	R–8	R–9
2-Methyl	46	71	67							
3-Methyl	54	29	33							
2-Ethyl				25		15	40			
3-Ethyl				10		?	<5			
2,5-Dimethyl				30		60	20			
2,4-Dimethyl				15		?	20	10		
2,3-Dimethyl				20	55	20	20	80	15	
3,4-Dimethyl					45	?		10	35	
2-*iso*Propyl									5	trace
3-*iso*Propyl									5	
2-*n*-Propyl									10	
2-Methyl-5-ethyl									40	10
2,3,4-Trimethyl										45
2,3,5-Trimethyl										45

TABLE IX

Thiophenes Boiling up to 166° in Gasoline Cut, Thermally Cracked Alberta Bitumen (R-Distillation)

Alkylthiophene	Wt % of total gasoline cut	% of total S in gasoline cut
Thiophene	0·32	4·9
2-Methyl	1·00	13·1
3-Methyl	0·50	6·6
2-Ethyl	0·54	6·3
3-Ethyl	0·07	0·8
2,5-Dimethyl	0·27	3·1
2,4-Dimethyl	0·34	3·9
2,3-Dimethyl	0·80	9·2
3,4-Dimethyl	0·16	1·8
2-*iso*Propyl	0·01	0·1
3-*iso*Propyl	0·01	0·1
2-*n*-Propyl	0·03	0·3
2-Methyl-5-ethyl	0·31	3·1
2,3,4-Trimethyl	>0·82	>8·4
2,3,5-Trimethyl	>0·82	>8·4
Total	6·0	70

In some ways the above results are similar to those obtained by Kinney, Smith, and Ball [14] for the thiophenic constituents in shale-oil naphtha. These

authors also detected all possible isomers up to the C_6 thiophenes, although they were not able to identify 2,4-dimethylthiophene with certainty. Since cracking temperatures alone affect the abundance of specific isomers to a marked degree,[18] it is not surprising that their quantitative estimates varied from ours. They too, however, found that among monosubstituted isomers the 2-position was favoured. Undoubtedly in the present case the thiophenes under discussion were formed by the cracking of larger molecular units existing in the original bitumen. Such similarities as exist suggest that the thiophenes in the shale-oil may well have been formed by a similar cracking process.

(4) *Sulphur Group Analysis*

The classes of non-thiophenic sulphur compounds in the low-boiling range under discussion are in all probability confined to mercaptans, sulphides, and disulphides. It was attempted to obtain estimates of these sulphur groups with a view at least to establishing upper limits. The problems of exact analysis of sulphur groups in cracked distillates have so far presented considerable difficulty.[19]

Mercaptans were titrated potentiometrically with fairly high accuracy,[20] although, as shown earlier by Ball,[19] their concentration decreased markedly with time. Sulphides were determined by forming an iodine complex and measuring its absorption near a maximum in the ultra-violet.[21–23] Because of interference from aromatics, thiophenes, and olefins, which could be estimated only approximately, accuracy was of the order of 20 per cent. Disulphides were reduced to mercaptans with zinc and acetic acid.[19] Results were not expected to be better than one-half order of magnitude.

Suffice it to summarize the results for the fairly typical R-series (see Table III).

Mercaptans were encountered in the range 0–40 p.p.m. S in fresh samples with the exception of a few of the higher fractions with up to ten times this amount. After four months this had decreased to zero in all but the last fraction. Not enough material remained for further analyses of R–1. Sulphides in R–2 to R–16 varied from 0·01 to 0·08 per cent S. Disulphides were found only in fractions R–10 to R–16 and varied from 10 to 80 p.p.m. S.

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SOME OBSERVATIONS CONCERNING THE VISCOSITY–TEMPERATURE BEHAVIOUR OF HYDROCARBONS *

By W. C. WINNING † (Fellow)

EVER since the classical studies of Thorpe and Rodger [1] in the 1890's investigation of the viscosity–temperature behaviour of hydrocarbons has been the vocation or avocation of uncounted workers. A large collection of data has been assembled and much effort has been directed to establishing underlying behaviour patterns. Nevertheless, few generalizations have emerged in a sufficiently specific form for practical mathematical application. Gaps and uncertainties in the data have long made sweeping analyses difficult.

Recently, however, Grunberg and Nissan [3] reworked and published all the hydrocarbon data they had collected in an exhaustive literature search. Further information has since been provided by the report of API Research Project No. 42,[2] which gives particularly complete and reliable data on the *n*-paraffins. In consequence, enough information is now available regarding several hydrocarbon families in which the writer has attempted to identify some characteristics which interrelate viscosity–temperature behaviour. This paper presents preliminary observations which may warrant fuller study in the years ahead.

The interrelationship of the *n*-alkanes, as represented by the *n*-paraffins, *n*-alkyl benzenes, *n*-alkyl *cyclo*pentanes, and *n*-alkyl *cyclo*hexanes, is demonstrated in Fig 1 for temperatures ranging from 32° to 210° F. The abscissæ are the viscosities at 140° F; the ordinates are the corresponding viscosities at the temperatures indicated. The scales are logarithmic and viscosities are in centistokes. All the pertinent data given in the references cited are included.

Three observations emerge on examination of Fig 1:

(1) The points for all four hydrocarbon classes have approximately the same scatter about the correlation lines. For preliminary purposes, therefore, the viscosity–temperature behaviour of these *n*-alkanes can be considered as identical over the range studied, except for the lowest members.

(2) On log–log co-ordinates this behaviour can be represented by straight lines.

(3) These straight lines converge to a common point, thus giving rise to the general equation:

$$\frac{P - \log V_a}{P - \log V_b} = R_{ab} \quad . \quad . \quad (1)$$

where V_a and V_b are the kinematic viscosities at temperatures, T_a and T_b; P is the convergence pole whose value is found to be −0·93; ‡ and R_{ab} is a ratio which varies with the temperatures being compared. Values of R_{ab} read from Fig 1 are listed in Table I.

TABLE I

Variation of R_{ab} with Temperature

T_a	T_b	R_{ab}
32	140	1·480
68	140	1·266
102	140	1·126
140	140	1·000
176	140	0·902
210	140	0·827

For comparisons at temperatures other than those of Table I it is helpful to have a rule for the variation of R_{ab} with the temperature, T_a. General experience indicates that this should approximate a reciprocal relationship, and therefore $1/R$ has been plotted *v.* temperature in Fig 2. Over the range 100° and 210°F the points fall on a straight line conforming to the equation:

$$1/R_{ab} = (T_a + 195)/335 \quad . \quad . \quad (2)$$

when $T_b = 140$. Thus for this range it becomes possible to write:

$$\frac{0{\cdot}93 + \log V_a}{0{\cdot}93 + \log V_b} = \frac{T_b + 195}{T_a + 195} \quad . \quad (3)$$

or

$$0{\cdot}93 + \log V = C/(T + 195) \quad . \quad (4)$$

Below 100° F the equation becomes unreliable.

An expression of the temperature function covering the full range of Table I could, of course, be estimated by the method of multiple regressions, but such a mathematical complication is not required to develop the conclusions of this paper.

Equation (3), which was derived for the *n*-alkanes, must somehow fall within a broader pattern which includes all hydrocarbons. Such a broader pattern would be represented, for instance, by:

$$P + \log V = C(T + S)^{-Q} \quad . \quad (5)$$

* MS received 21 July 1958. † Standard Oil Company (New Jersey). ‡ Logarithm base 10.

An equation of this sort is obviously extremely flexible, and could be expected to reproduce a wide variety of viscosity–temperature curves with fair accuracy. If it were furthermore found that two of the three constants, P, Q, and S, are substantially the same for all hydrocarbons, then equation (5) would only case left to examine now is that of letting Q vary. In this event equation (5) becomes:

$$0{\cdot}93 + \log V = C(T + 195)^{-Q} \quad . \quad (6)$$

or

$$\log (0{\cdot}93 + \log V) = \log C - Q \log (T + 195) \quad (7)$$

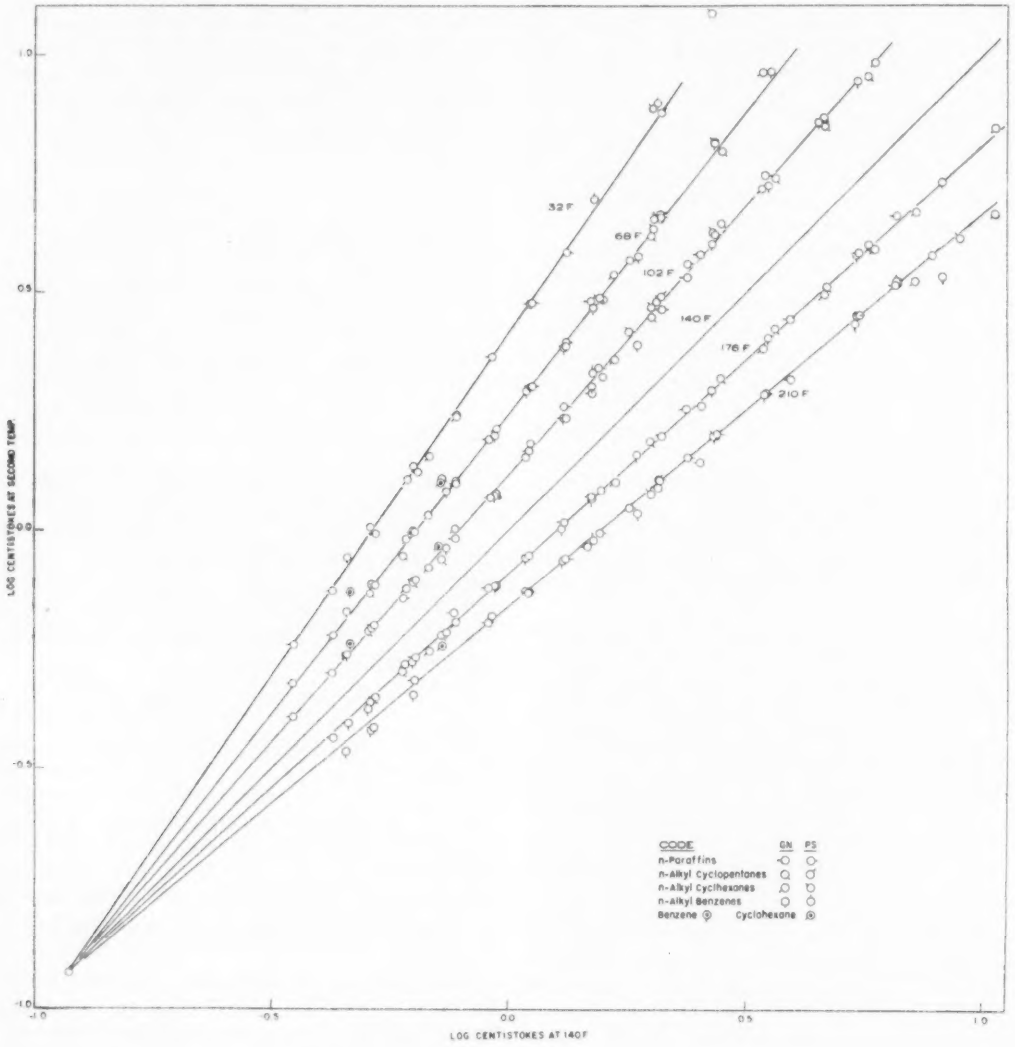


Fig 1

tie all hydrocarbon viscosity–temperature behaviour to that of n-alkanes by the single remaining variable.

Some time ago Sloane and Winning [4] tested the case where $Q = 1$ on a variety of hydrocarbon lubricating oils. Their findings eliminated the possibility of holding either P at 0·93 or S at 195 as required by equation (4), when Q is fixed at 1. Consequently, the

To test equation (7), the plot shown in Fig 3 was prepared. Ordinates are units of log (0·93 + log V), abscissæ of log (T + 195), corresponding to the viscosities and temperatures indicated.

When n-alkane characteristics are read from the curves of Fig 1 and plotted on the co-ordinates of Fig 3, straight lines with a slope (Q) of 1·00 result. This

is a necessary consequence of the derivation of the chart and is evidence only that the chart has been constructed in correct accord with this derivation.

Furthermore, when data for 0 and 100 V.I.* oils, read off the ASTM viscosity temperature chart, [6] are plotted as in Fig 3, straight lines are also obtained. This is the result hoped for and demonstrates that

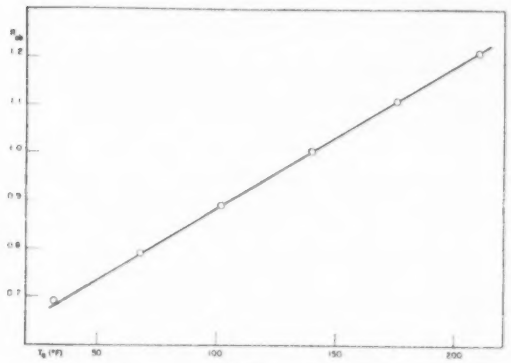


FIG 2

VARIATION OF $1/R_{ab}$ WITH T_a WHEN T_b IS 140° F

equation (7) is applicable from 100° to 210° F to the commercial lubricating oils for which the ASTM chart is designed. Furthermore, if the ASTM chart is accepted as having general application to all hydrocarbons, then the same should be true of equation (7). Thus it seems possible to characterize the viscosity–temperature behaviour of all hydrocarbons over the range 100°–210° F by an equation containing only two independent variables, one which represents the particular hydrocarbon and the other a factor which relates the behaviour to that of the *n*-alkanes.

This factor, Q, deserves some examination. It is related to the actual viscosity–temperature slope, dV/dT, by:

$$Q = \frac{T + 195}{V\,(0{\cdot}93 + \log V)} \cdot \frac{dV}{dT} \quad . \quad (8)$$

If we represent the *n*-alkanes by the subscript n, and any other hydrocarbon by m, then, since $Q_n = 1$:

$$Q_m = \frac{Q_m}{1} = \frac{Q_m}{Q_n} = \frac{\dfrac{T_m + 195}{V_m\,(0{\cdot}93 + \log V_m)} \cdot (dV/dT)_m}{\dfrac{T_n + 195}{V_n\,(0{\cdot}93 + \log V_n)} \cdot (dV/dT)_n} \quad . \quad . \quad (9)$$

Suppose the two slopes are compared at a common point. In this case $V_m = V_n$, $T_m = T_n$ and:

$$Q_m = \frac{(dV/dT)_m}{(dV/dT)_n} \quad . \quad . \quad (10)$$

Thus Q is the ratio of the viscosity–temperature slope, dV/dT, of the hydrocarbon to that of the hypothetical *n*-alkane which possesses the same viscosity at the temperature of comparison.

This analysis can be carried further. For instance, by strictly theoretical reasoning Eyring [5] has derived an equation for viscosity–temperature behaviour which may be represented as:

$$\log V = \frac{E}{kT} + \log (NhM) \quad . \quad (11)$$

where k is the Boltzman constant, N is Avogadro's number, h is the Planck constant, and M the

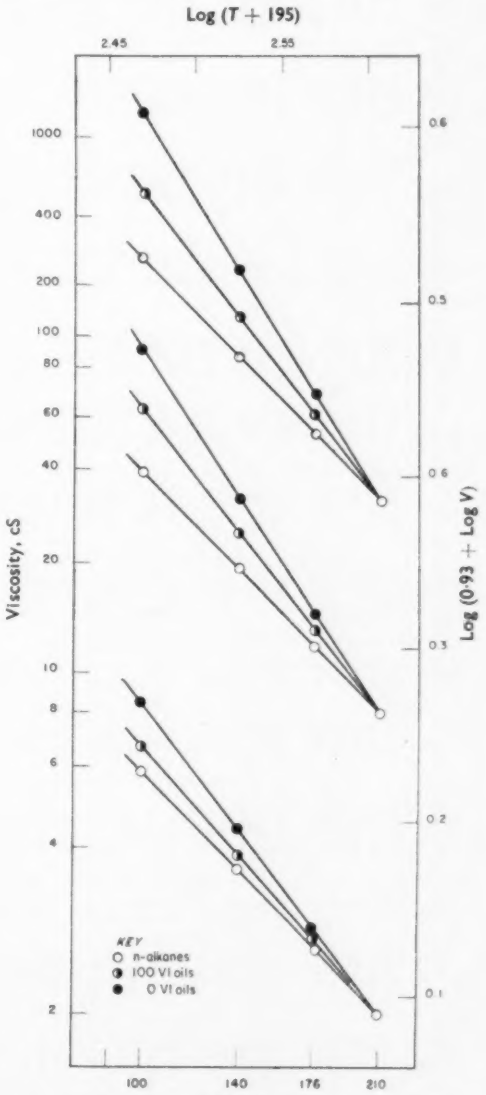


FIG 3

VISCOSITY–TEMPERATURE CURVES

* The V.I. is mentioned only to indicate that the data are representative of practical conditions. It plays no part in the proof.

TABLE II

Viscosity Conversion Chart

Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *	Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *	Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *	Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *	Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *	Visc., cS (V)	Log (0·93 + log V) / (W)	W / 0·138 *
0·20	−0·636	−4·61	1·0	−0·032	−0·23	6·0	0·232	1·69	60	0·433	3·14	2,000	0·626	4·55	300,000	0·807	5·86
0·22	−0·565	−4·09	1·1	−0·012	−0·09	6·2	0·236	1·71	65	0·438	3·18	2,200	0·630	4·57	350,000	0·811	5·89
0·24	−0·509	−3·69	1·2	0·004	0·03	6·4	0·240	1·74	70	0·443	3·22	2,400	0·634	4·60			
0·26	−0·462	−3·35	1·3	0·019	0·14	6·6	0·243	1·76	75	0·448	3·25	2,600	0·638	4·63	400,000	0·815	5·92
0·28	−0·424	−3·07	1·4	0·032	0·23	6·8	0·246	1·79				2,800	0·641	4·65	500,000	0·821	5·96
									80	0·452	3·28				600,000	0·827	6·00
0·30	−0·390	−2·83	1·5	0·044	0·32	7·0	0·249	1·81	85	0·456	3·31	3,000	0·644	4·67			
0·32	−0·362	−2·62	1·6	0·055	0·40	7·5	0·256	1·86	90	0·460	3·34	3,500	0·651	4·72	700,000	0·831	6·04
0·34	−0·336	−2·44	1·7	0·064	0·47				95	0·464	3·37	4,000	0·656	4·76	800,000	0·835	6·07
0·36	−0·313	−2·27	1·8	0·074	0·54	8·0	0·263	1·91				4,500	0·661	4·80	900,000	0·838	6·09
0·38	−0·292	−2·12	1·9	0·082	0·60	8·5	0·269	1·95	100	0·467	3·39						
									110	0·473	3·43	5,000	0·665	4·83	1,000,000	0·841	6·11
0·40	−0·274	−1·98	2·0	0·090	0·65	9·0	0·275	2·00	120	0·478	3·47	5,500	0·669	4·85	1,200,000	0·846	6·14
0·42	−0·257	−1·86	2·1	0·097	0·70	9·5	0·281	2·04	130	0·483	3·51	6,000	0·673	4·88	1,400,000	0·850	6·17
0·44	−0·242	−1·75	2·2	0·104	0·75							6,500	0·676	4·91	1,600,000	0·853	6·20
0·46	−0·227	−1·65	2·3	0·111	0·80	10·0	0·286	2·08	140	0·488	3·54				1,800,000	0·856	6·22
0·48	−0·214	−1·55	2·4	0·117	0·85	10·5	0·291	2·11	150	0·492	3·57	7,000	0·679	4·93			
									160	0·496	3·60	8,000	0·684	4·97	2,000,000	0·859	6·24
0·50	−0·201	−1·46	2·5	0·123	0·89	11·0	0·295	2·14	180	0·503	3·65	9,000	0·689	5·00	2,500,000	0·865	6·28
0·52	−0·190	−1·38	2·6	0·129	0·93	12·0	0·303	2·20									
0·55	−0·174	−1·26	2·7	0·134	0·97	13·0	0·310	2·25	200	0·509	3·69	10,000	0·693	5·03	3,000,000	0·870	6·32
0·60	−0·150	−1·09	2·8	0·139	1·01	14·0	0·317	2·30	220	0·515	3·73	12,000	0·700	5·08	4,000,000	0·877	6·37
0·65	−0·129	−0·93	2·9	0·144	1·05				240	0·520	3·77	14,000	0·706	5·13	5,000,000	0·882	6·41
						15·0	0·323	2·35	260	0·524	3·81	16,000	0·711	5·16			
0·70	−0·111	−0·80	3·0	0·148	1·08	16·0	0·329	2·39	280	0·528	3·84	18,000	0·715	5·19	6,000,000	0·887	6·44
0·75	−0·094	−0·68	3·2	0·157	1·14	17·0	0·334	2·43							7,000,000	0·891	6·47
0·80	−0·079	−0·57	3·4	0·165	1·20	18·0	0·339	2·47	300	0·532	3·87	20,000	0·719	5·22	8,000,000	0·894	6·49
0·85	−0·066	−0·48	3·6	0·172	1·25	19·0	0·344	2·50	350	0·541	3·93	22,000	0·722	5·24			
0·90	−0·054	−0·39	3·8	0·179	1·30				400	0·548	3·98	25,000	0·727	5·28	9,000,000	0·897	6·51
0·95	−0·042	−0·30				20·0	0·349	2·54	450	0·554	4·02				10,000,000	0·899	6·53
			4·0	0·185	1·35	21·0	0·353	2·56				30,000	0·733	5·32			
			4·2	0·191	1·39	22·0	0·356	2·58	500	0·560	4·07	35,000	0·738	5·36			
			4·4	0·197	1·43	23·0	0·360	2·61	550	0·565	4·11	40,000	0·743	5·39			
			4·6	0·202	1·47				600	0·569	4·14	45,000	0·747	5·42			
			4·8	0·207	1·50	24·0	0·364	2·64	650	0·573	4·17						
						26·0	0·370	2·68				50,000	0·750	5·45			
			5·0	0·212	1·54	28·0	0·376	2·72	700	0·577	4·19	60,000	0·756	5·50			
			5·2	0·216	1·57				800	0·583	4·23	70,000	0·762	5·54			
			5·4	0·221	1·60	30·0	0·381	2·76	900	0·589	4·27	80,000	0·766	5·57			
			5·6	0·225	1·63	32·0	0·386	2·80				90,000	0·770	5·59			
			5·8	0·229	1·66	34·0	0·391	2·84	1,000	0·594	4·31						
						36·0	0·396	2·88	1,100	0·599	4·35	100,000	0·773	5·61			
						38·0	0·400	2·91	1,200	0·603	4·38	120,000	0·779	5·65			
									1,300	0·607	4·40	140,000	0·784	5·69			
						40·0	0·403	2·93				160,000	0·788	5·72			
						42·0	0·407	2·96	1,400	0·610	4·42	180,000	0·791	5·75			
						45·0	0·412	2·99	1,500	0·613	4·44						
									1,600	0·616	4·46	200,000	0·795	5·77			
						50·0	0·420	3·05	1,800	0·622	4·51	250,000	0·801	5·82			
						55·0	0·427	3·10									

* $\frac{W}{0{\cdot}138} = \frac{W}{Z_b - Z_a}$ where $a = 100°\text{F}$ $b = 210°\text{F}$

molecular weight. E is the activation energy which varies somewhat with temperature but for a limited range of temperature one can write:

$$\frac{dV}{dT} = -\frac{EV}{kT^2} \quad . \quad . \quad (11a)$$

Using subscripts as before we obtain:

$$\frac{(dV/dT)_m}{(dV/dT)_n} = \frac{E_m}{E_n} \quad . \quad . \quad (12)$$

when comparison is made at the same temperature and viscosity. Hence

$$Q_m = \frac{E_m}{E_n} \quad . \quad . \quad (12a)$$

That is, Q is a measure of the energy of activation of any hydrocarbon relative to that of the hypothetical n-alkane which has the same viscosity at the temperature involved. Other associations of Q can doubtless be developed.

In each instance Q is a measure of some aspect of viscosity–temperature behaviour *relative* to that of the n-alkanes. Q is therefore a magnitude which has an absolute significance independent of the empirical approach by which it has been derived. The particular contribution of the foregoing analysis has been to demonstrate that Q, and all the relationships it implies for any particular hydrocarbon or hydrocarbon mixture, approximate a constant value over the 100°–210° F temperature range.

The question arises as to how Q varies as hydrocarbon structure departs from that of the n-alkanes. To assist in such calculations Table II lists values of log (0·93 + log V) corresponding to viscosities ranging from 0·2 to 10,000,000 cS. Furthermore, since:

$$-Q = \frac{W_a - W_b}{Z_a - Z_b} \quad . \quad . \quad (13)$$

where $W = \log\ (0{\cdot}93 + \log\ V)$, $Z = \log\ (T + 195)$ and subscripts a and b refer to the temperatures, one can write:

$$Q = \frac{W_a}{Z_b - Z_a} - \frac{W_b}{Z_b - Z_a} \quad . \quad (13a)$$

The additional column of Table II gives values of $W/(Z_b - Z_a)$ where the temperatures are 100° and 210° F. These figures permit the estimation of Q by a single subtraction from viscosity data at 100° and 210° F.

Calculating Q for a series of *iso*paraffins reported by API Project No. 42 [2] gives the results of Table III. Here it is apparent that the presence of a side chain increases Q, that the effect of the side chain increases as it moves towards the centre of the molecule, and that a maximum effect is produced by side chains 3 to 8 carbons in length.

Multiplying the number of side chains markedly raises Q, as indicated by Table IV. Phenyl groups increase Q more than alkyl in complex structures, and *cyclo*hexyl groups have a still greater effect according to Table V. Here a definite maximum value of Q appears when all three groups joined to the central carbon contain 6 carbons. This appears to be an effect of symmetry which can also be detected in Table III.

TABLE III

Viscosity Behaviour of iso*Paraffins*

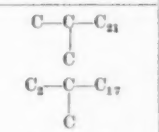
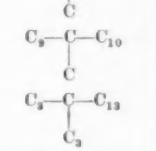
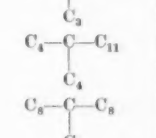
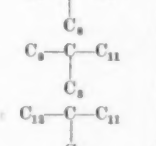
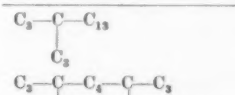
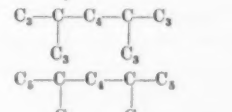
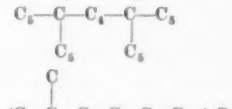
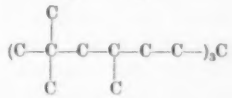
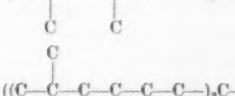
Compound	Viscosity cS at 210° F	Q
	2·85	1·01
	2·14	1·02
	2·00	1·05
	1·67	1·08
	1·69	1·08
	2·48	1·11
	3·09	1·09
	4·9	1·07

TABLE IV

Effect of Additional Side Chains

Compound	Viscosity, cS at 210° F	Q
	1·67	1·08
	1·25	1·15
	2·72	1·20
	4·0	1·30
	10·7	1·38

Higher values of Q are therefore indicative of increasing departures from linearity, or of increasing skewness, and Q is a measure of this non-linearity. Obviously, non-linearity is not well defined as a positive concept, and to give it quantitative significance we shall assume that two hydrocarbons are non-linear to the same degree when both have the same Q.

TABLE V

Effect of Ring Structures

Compound	Viscosity, cS at 210° F	Q
$C_6-\underset{\underset{C}{\vert}}{C}-C_6$	0·91	1·03
(ph)—$\underset{\underset{C}{\vert}}{C}$—(ph)	1·15	1·01
(ch)—$\underset{\underset{C}{\vert}}{C}$—(ch)	1·76	1·11
$C_6-\underset{\underset{C_6}{\vert}}{C}-C_6$	1·51	1·11
(ph)—$\underset{\underset{C_6}{\vert}}{C}$—(ph)	2·00	1·29
(ch)—$\underset{\underset{C_6}{\vert}}{C}$—(ch)	3·08	1·41
$C_6-\underset{\underset{C_{13}}{\vert}}{C}-C_6$	2·84	1·09
(ph)—$\underset{\underset{C_{13}}{\vert}}{C}$—(ph)	3·7	1·22
(ch)—$\underset{\underset{C_{13}}{\vert}}{C}$—(ch)	5·3	1·30

(ph) = phenyl (ch) = *cyclo*hexyl

It is not intended to make a definitive study of the effect of structure in this paper. However, enough data have been presented here to demonstrate that the effect is exceedingly complex, varying not only with the size, nature, and location of substituent groups, but that various maxima are reached or passed through. Hence a common value of Q is not evidence that a number of hydrocarbons chosen at random are alike chemically, only that, by our definition, they are non-linear to the same degree.

Despite the wide variety of structures which may be characterized by a particular value of Q, it does seem possible that when dealing with very complex mixtures such as lubricating oils there will be an averaging effect so that a common Q rating is evidence of a substantial degree of homology. Obviously this hypothesis is not readily susceptible to proof, but it may be interesting to observe the variation in Q of such a widely accepted basis for lubricating oil classification as the Dean and Davis viscosity index.[6]

Table VI indicates that for viscosities of over 8 cS at 210° F the value of Q, and hence the non-linearity of the 100 V.I. series, is substantially constant. This constancy is perhaps evidence of homology within 100 V.I. oils, but even if the evidence is accepted considerable question remains as to what such homology, or constant non-linearity, may mean in terms of specific physical and chemical structure.

TABLE VI

Q Rating of V.I. Standards

Viscosity, cS at 210° F	Standard Series	
	100 V.I.	0 V.I.
2·0	1·12	1·29
4·0	1·21	1·37
8·0	1·27	1·54
16·0	1·27	1·58
32·0	1·28	1·62
64·0	1·29	1·65

Below 8 cS the value of Q falls rapidly and the 100 V.I. series approaches the *n*-alkanes. Thus there is a marked break in the homogeneity of the Pennsylvania crudes from which the 100 V.I. standards are derived. This break is of course well known to all students of viscosity index scales and the variation in Q is consistent with this knowledge.

The 0 V.I. series shows a similar break in the low viscosity range. However, above 8 cS Q still increases, though less rapidly, as viscosity rises. Hence the 0 V.I. series appears to lack the homology which characterizes the 100 V.I. in the upper viscosity range.

However uncertain the exact relation of values of Q above 1 may be to molecular structure, the significance of 1 itself appears quite well established, at least for individual hydrocarbons. A Q of 1 is characteristic of the normal methylene chain, either alone or containing only substituent groups which do not significantly alter its cross-sectional dimensions or its linearity.

Furthermore, upon examination of viscosity data for many hydrocarbons the writer found no instances of a Q significantly below 1. Hence it seems that the *n*-alkanes define the boundary of minimum temperature sensitivity of hydrocarbons. This concept of boundary viscosity–temperature characteristics is not new and was employed by Sanderson [7], for instance, as the basis of his Relative Viscosity–Temperature Numbers. However, Sanderson included data on oxygenated compounds in drawing up his reference series, and his conclusions are therefore not directly comparable to those of this study.

It is not to be inferred that substances lower in viscosity–temperature sensitivity than *n*-alkanes are

non-existent. Fenske,[8] for instance, has pointed to polymethyl silicones ranging from 0·33 to 0·83 in Q. Evans [9] has cited orthosilicates:

n-Butyl .	. 0·86
n-Hexyl .	. 0·89
n-Heptyl .	. 0·90

Wright [10] refers to polymethyl siloxanes far less temperature-sensitive than the *n*-alkanes.

These figures are calculated from viscosities at 100° and 210° F. Whether the silicon compounds can actually be related to the *n*-alkanes in viscosity–temperature behaviour by a coefficient such as Q is still to be established.

This paper, as stated earlier, is presented as a preliminary study. The observations put forward require extension over a wider range of temperatures, viscosities, and hydrocarbon types. Oxygen, halogen, silicon, sulphur, and phosphorus-containing derivatives of hydrocarbons need to be tied in, and so do solutions of high molecular weight polymers. A more exact expression for Z, the temperature function, is needed and the limitations of 0·93 as the value of P, in W the viscosity function, deserve study. The writer hopes that the relatively brief observations of this paper will encourage others to make more definitive investigations along the lines indicated.

CONCLUSIONS

(1) Over the range 32°–210° F, the viscosity temperature of the *n*-alkanes, as represented by the *n*-paraffins, *n*-alkyl benzenes, *n*-alkyl *cyclo*pentanes, and *n*-alkyl *cyclo*hexanes, can be written as a single equation:

$$W = C - QZ \quad . \quad . \quad (13)$$

where $Q = 1$

and W is a function of viscosity such that:

$$W = \log (0{\cdot}93 + \log V)$$

C is a constant characterizing the particular hydrocarbon.

Z is a function of temperature and over the range 100°–210° F may be approximated by:

$$Z = \log (T + 195)$$

(2) Over the 100°–210° F range all hydrocarbons and their mixtures may be represented by the same equation (13). The viscosity and temperature functions, W and Z, remain unchanged but Q may range upward from 1.

(3) Hence the viscosity–temperature behaviour of the normal methylene chain as represented by the *n*-alkanes sets a basic pattern to which the behaviour of other hydrocarbons may be related by the single coefficient Q.

(4) The physical significance of Q is not limited to equation (13). It is a general measure of viscosity–temperature behaviour relative to that of *n*-alkanes. For instance, Q gives the ratio of the viscosity–temperature slope, dV/dT, of any hydrocarbon to that of the hypothetical *n*-alkane of the same viscosity at the temperature of comparison.

(5) In terms of hydrocarbon structure, Q is regarded as a measure of the non-linearity imparted by substituent groups to the basic normal methylene chain structure.

ACKNOWLEDGMENTS

The writer owes much to his friend E. B. Evans, whose long interest in this study has been a source of much stimulation. He is also greatly indebted to both his secretary and the Standard Oil Company (New Jersey), whose mutual indulgence materially facilitated the preparation of this paper.

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STUDIES IN SHALE OIL

PART IX. FURTHER DATA ON EMULSIONS AND SLUDGES*

By GEO. E. MAPSTONE† (Fellow)

SUMMARY

The sludge that accumulated in the crude oil storage tanks was stabilized by waxes, asphaltenes, and dust. Heating sufficiently allowed the waxes to melt and the asphaltenes to coagulate and settle out with the dust, thus allowing the sludge to be resolved.

INTRODUCTION

In the same way that petroleum crudes differ, so do shale oils, and methods of handling must be modified according to local requirements. The deposition of heavy sludges from oils which are not perfectly dry appears to be a characteristic of crude shale oils. It is the purpose of this paper to place on record some experiences with the sludges from South African crude shale oil and to indicate some differences between these and other shale oil sludges.

In general, this crude shale oil as received at the refinery from the carbonizing department has been settled and filtered and contains less than 0·2 per cent of water. However, much of this water settles in the crude oil storage tanks, which finally accumulate a heavy deposit of very viscous to semi-solid sludge containing about 50 per cent water. The appearance of this sludge is very similar to that of the Australian shale oil sludges described elsewhere.[1,2]

EXPERIMENTAL

Because of the known effects of acids and heat on the Australian sludges, these were tried on the present sludges.

When the sludge was heated to boiling the oil broke cleanly from the water while a quantity of asphaltenes coagulated and settled to the bottom of the water. On cooling to room temperature the oil set as a waxy cake.

TABLE I

Properties of Oils Recovered from Sludges

	Setting Pt, ° F	Asphaltenes, wt %	Sulphur, wt %
Original crude oil	59	6·63	0·65
Oil from sludge treated by:			
(1) Boiling with added water	94	2·88	—
(2) Boiling with 0·5% H_2SO_4	99	4·39	—
(3) Boiling alone: (*a*)	102	4·63	0·62
(*b*)	120	4·57	0·64
Asphaltenes from crude	—	—	0·76

Very similar results were obtained when the sludge was acidified and heated, the break occurring somewhat more quickly.

Since the very waxy character of the oils recovered from the sludge had not been reported before, the setting point, asphaltene, and sulphur contents of the recovered oils were determined (Table I).

An attempt to break the sludge in a storage tank by injecting live steam through the water drains was only partially successful due to the precipitated asphaltenes melting and sealing off the water drain. When cleaned out, this asphaltene deposit was of two kinds. Where it had been exposed to the steam it was hard and brittle, while those portions which had not been in contact with the steam were soft and flowed to assume the shape of the container. The analyses of the two types of asphaltene are given in Table II. A point of interest is that, when dried in the air oven at 100° C, both samples fused and coked. The results of successive Soxhlet extractions of a sample of the soft asphaltene are given in Table III. The ash present in the sample was mainly silica with small amounts of iron and magnesium.

TABLE II

Examination of Asphaltene Deposit from Sludge

Description	Hard	Soft
Solubility in CCl_4, wt %	25·1	12·8
Solubility in CS_2, wt %	36·9	43·3
Solubility in plant kerosine	—	90·0
Solubility in plant gas oil	—	90·3
Ash content	8·7	5·9
Penetration at 77° F	2	68
R & B softening point, ° F	170	114

The deposition of this asphaltene complicated the treatment of the sludge despite the high solubility of the deposit in the crude kerosine and gas oil streams from the plant (Table II). Dilution of the sludge with such oils did aid the breaking somewhat, but this was due to the reduction in the viscosity of the separated oil rather than to the solution of the asphaltene, as shown by the beneficial action of gasoline when the sludge was not actually boiled.

* MS received 6 May 1958.

† Present address:—Dermacult (S.A.) Pty. Ltd, Box 726, Johannesburg, South Africa. Formerly South African Torbanite Mining and Refining Co. Ltd.

Effective treatment of the sludge on the plant scale was achieved by heating it in a separate small tank from which the deposited asphaltenes could be removed from time to time. This deposit was fused solid and not granular, as was the deposit from the Australian sludge,[2] and so could not be handled in the same manner with scrapers. It was found that live steam injection was more effective than steam coils and, although actual boiling of the tank contents could not be observed, treatment was effective without the addition of solvent oils. Although the break was never quite complete, the amount of residual material left in the treatment tank to be re-treated varied little in volume, being generally much less than 5 per cent by volume of the tank contents, most of this volume being left to prevent remixing the separated oil and water.

TABLE III

Successive Soxhlet Extraction of Soft Asphaltenes

Solvent	Constituent	Weight per cent	
		Fraction	Cumulative
Petroleum ether (40°–60° C)	Malthenes	31·0	31·0
Carbon tetrachloride	Asphaltenes	34·8	65·8
Benzene	Asphaltenes	2·8	68·6
Carbon disulphide	Carbenes	24·1	70·7
	Carboids	25·1	95·8
	Ash	4·2	
	Total	100·0	

DISCUSSION

The data in Table I show that not only was the recovered oil more waxy than the original crude but that it also had a lower asphaltene content. The following theory, based on these observations, explains the formation of the sludge and its properties.

The temperature of the oil in the storage tanks is very close to its setting point and, under these circumstances, some of the harder waxes will have crystallized out. In addition, asphaltenes precipitating from the oils due to oxidation, supersaturation, or adsorption on the wax crystals will form an additional finely dispersed solid or semi-solid phase. The fact that the asphaltene content of the recovered oil is about 2 per cent less than that of the original crude oil suggests that incipient coagulation of initially colloidally dispersed asphaltenes is a significant factor. Any water emulsified or suspended in the oil will settle slowly, but the droplets would be strongly stabilized by the solids present, namely, wax crystals, asphaltenes, and dust. In time this emulsion will settle to the bottom of the tank, but, because of the high solids content, it will be quite stable and persist as sludge.

On heating this sludge the wax and asphaltenes would melt, the former redissolving in the oil, while the latter would entrain the dust as they coagulate and settle out. The removal of the solid phases then permits the resolution of the sludge to free the oil containing a higher than average wax content from the water while the asphaltenes collect as a tar below the water.

The slight improvement obtained when acid was used can be attributed to its action in assisting the coagulation of the asphaltenes and to its lowering the oil–water interfacial tension.[1]

The wax and semi-liquid or liquefiable asphaltenes in this sludge contrast with the solid " B.S." in the Australian sludges. In the former case heating alone can be effective in resolving the sludge completely, as the asphaltenes coagulate when heated sufficiently. In the latter case the coagulation of the " B.S." was effected by the acid polymerization of pyrroles, etc., in the oil.

ACKNOWLEDGMENT

The author wishes to acknowledge with thanks the permission granted by the management of the South African Torbanite Mining and Refining Company Ltd for permission to publish this paper.

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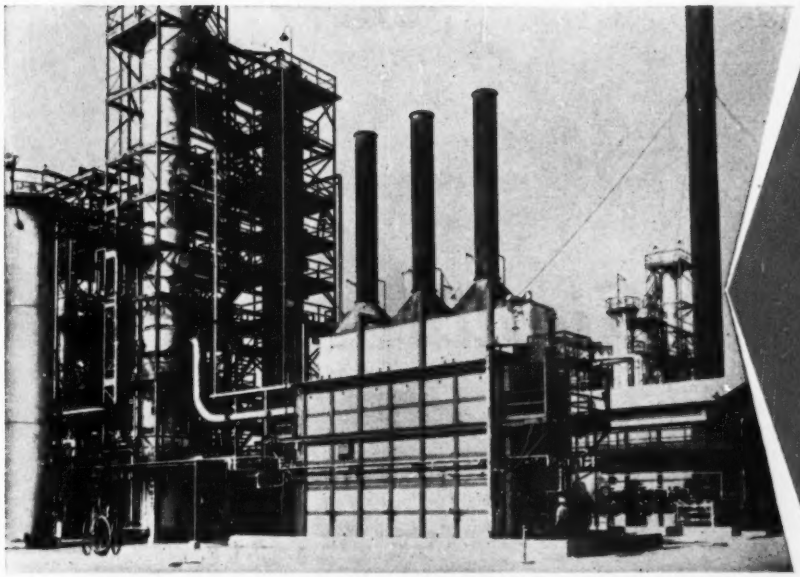

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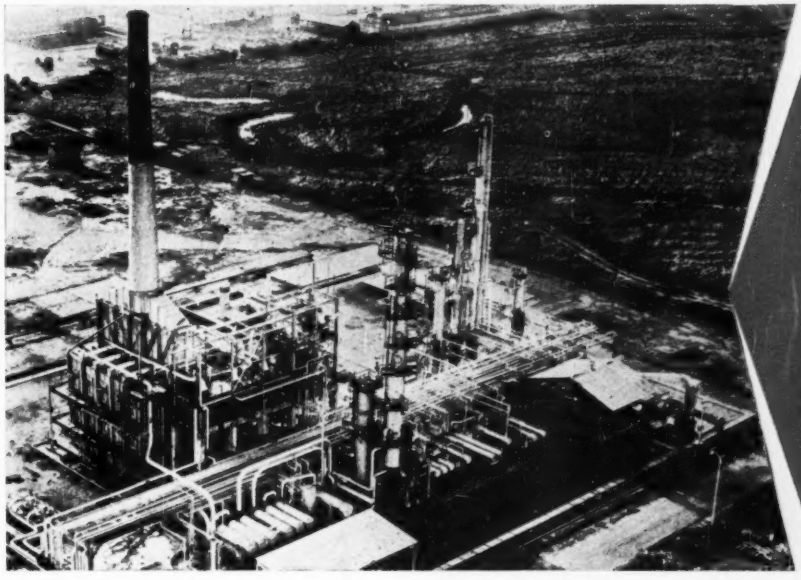

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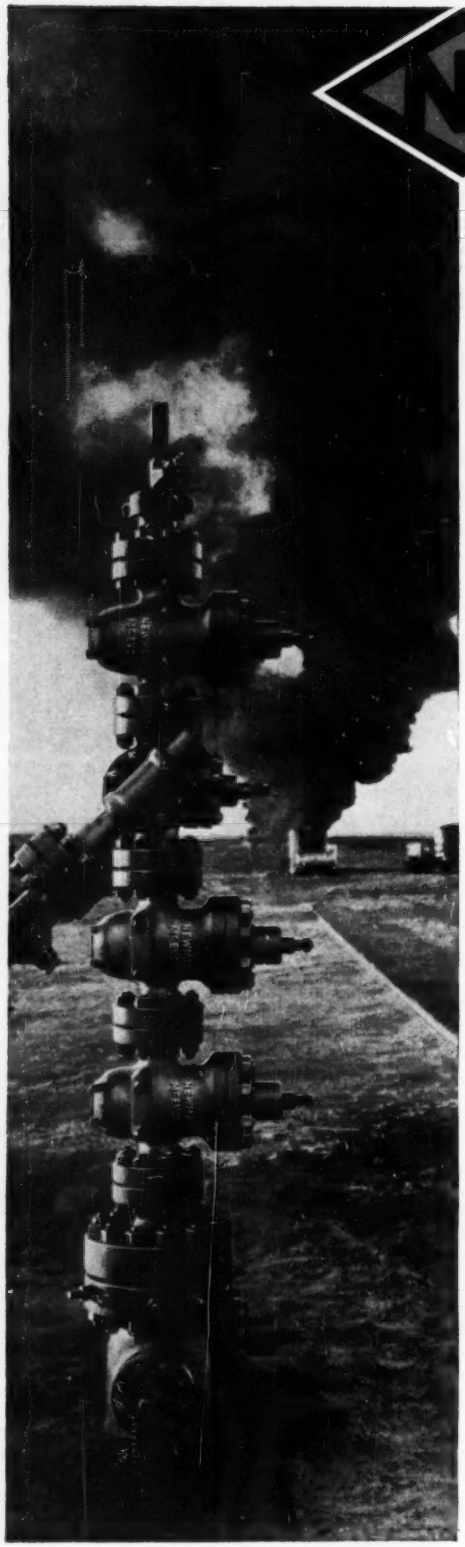

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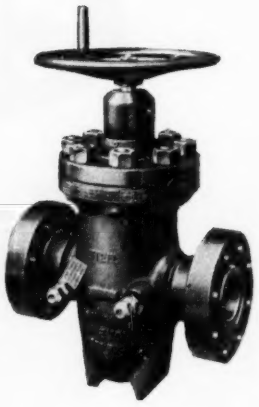

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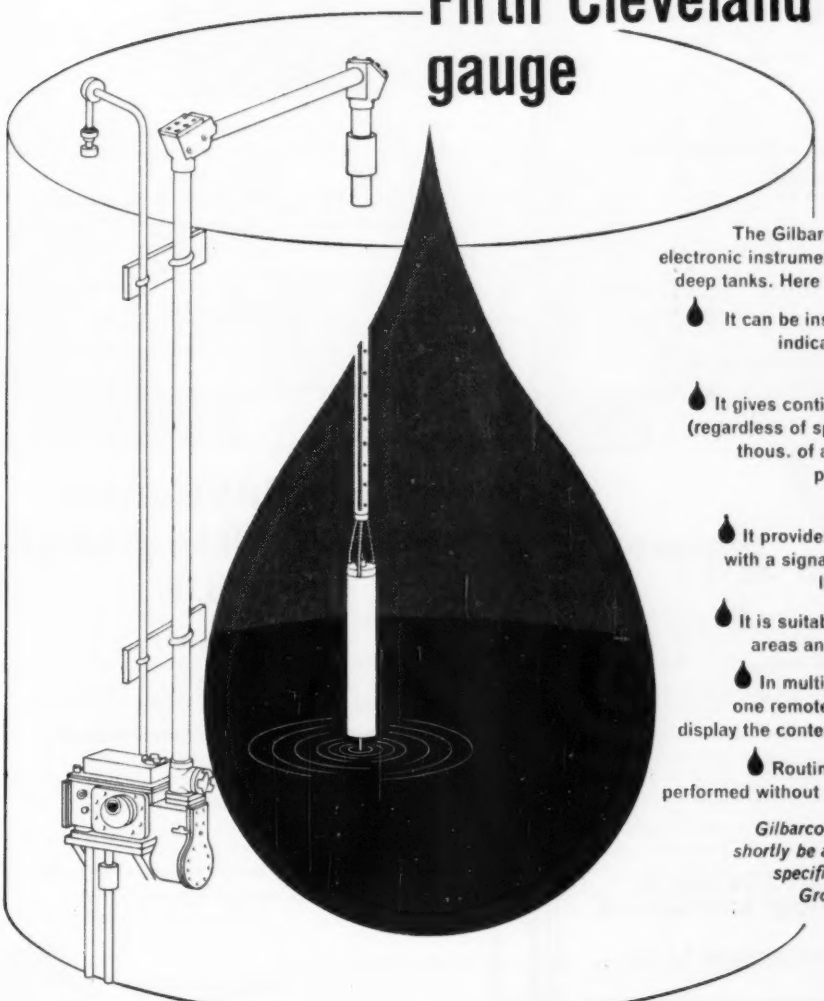

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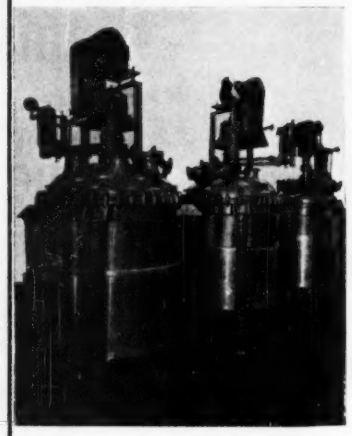

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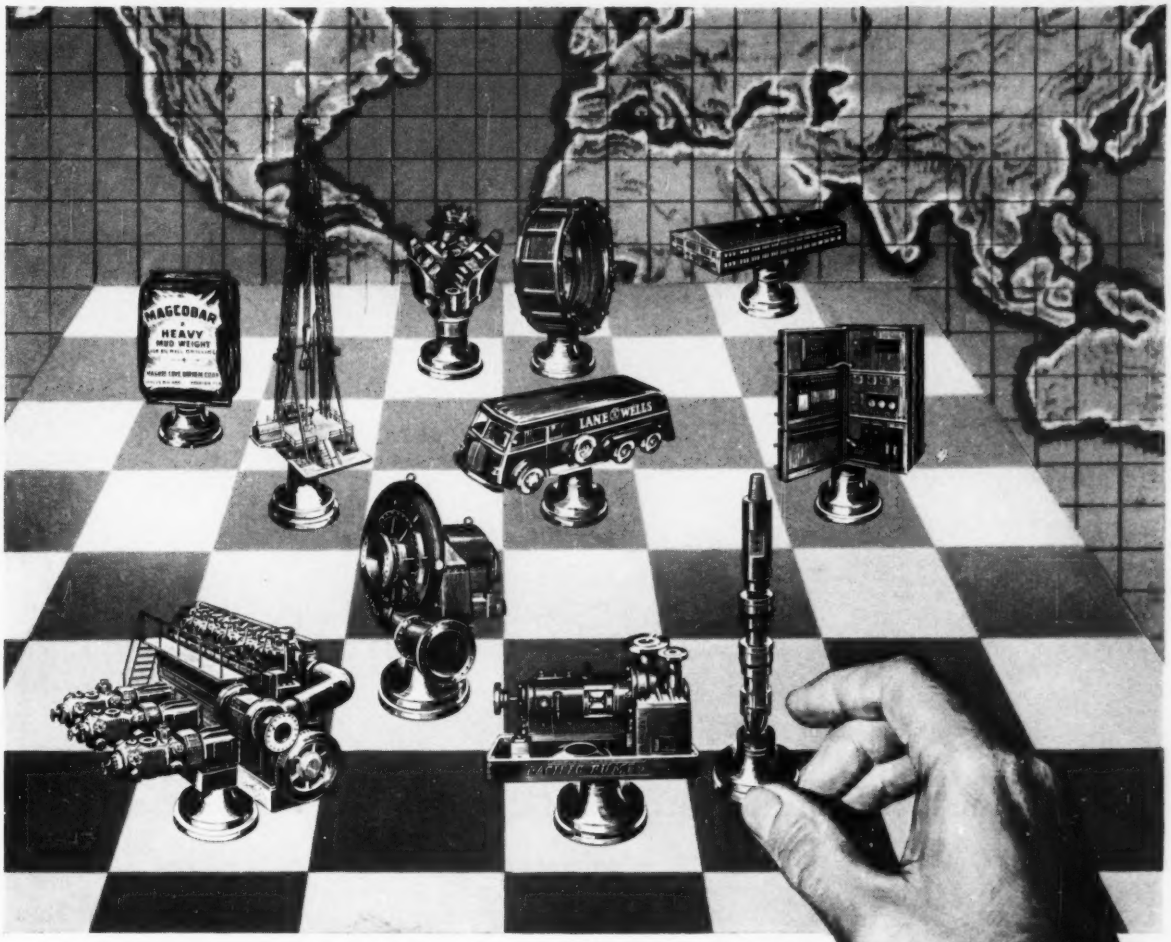

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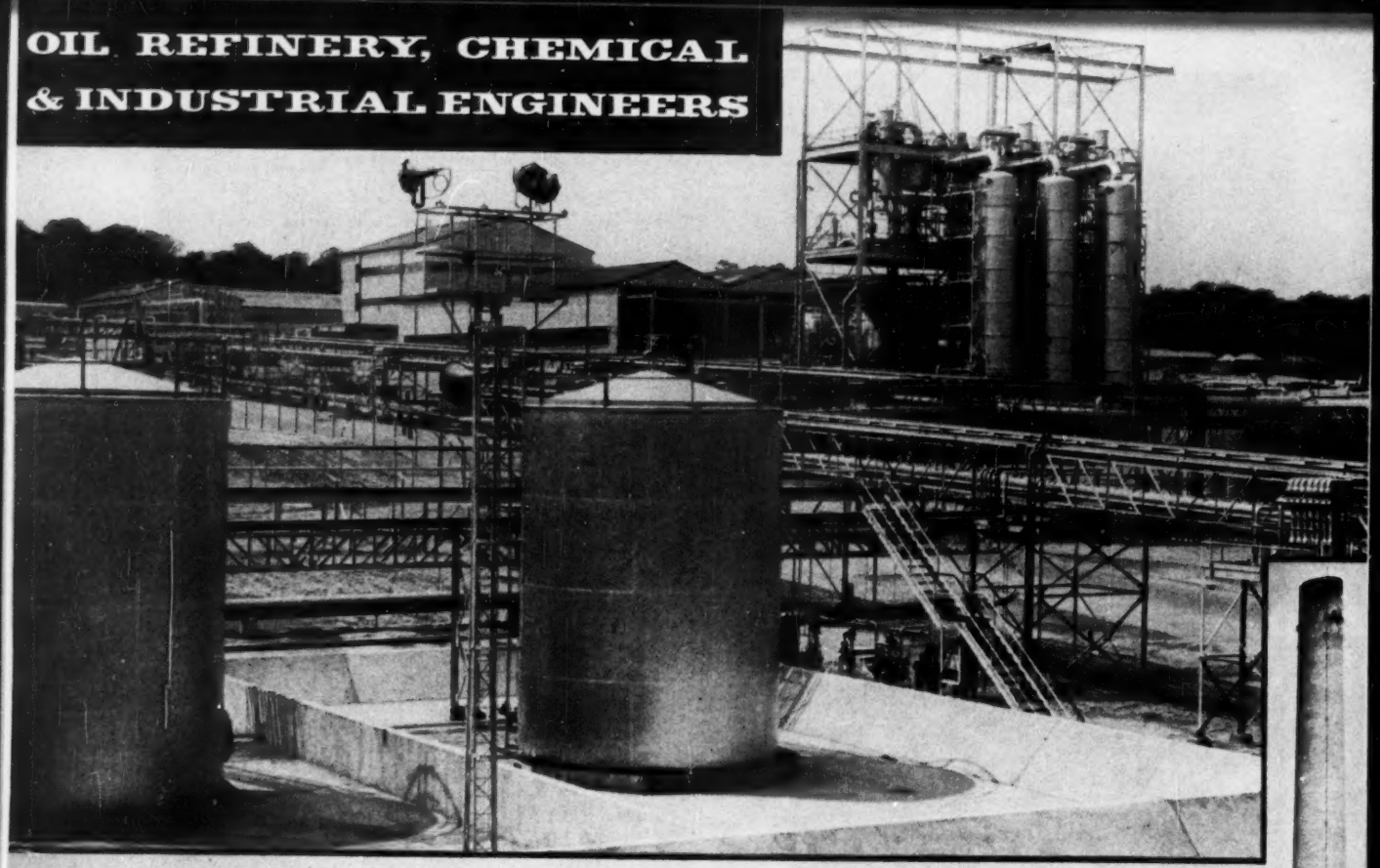

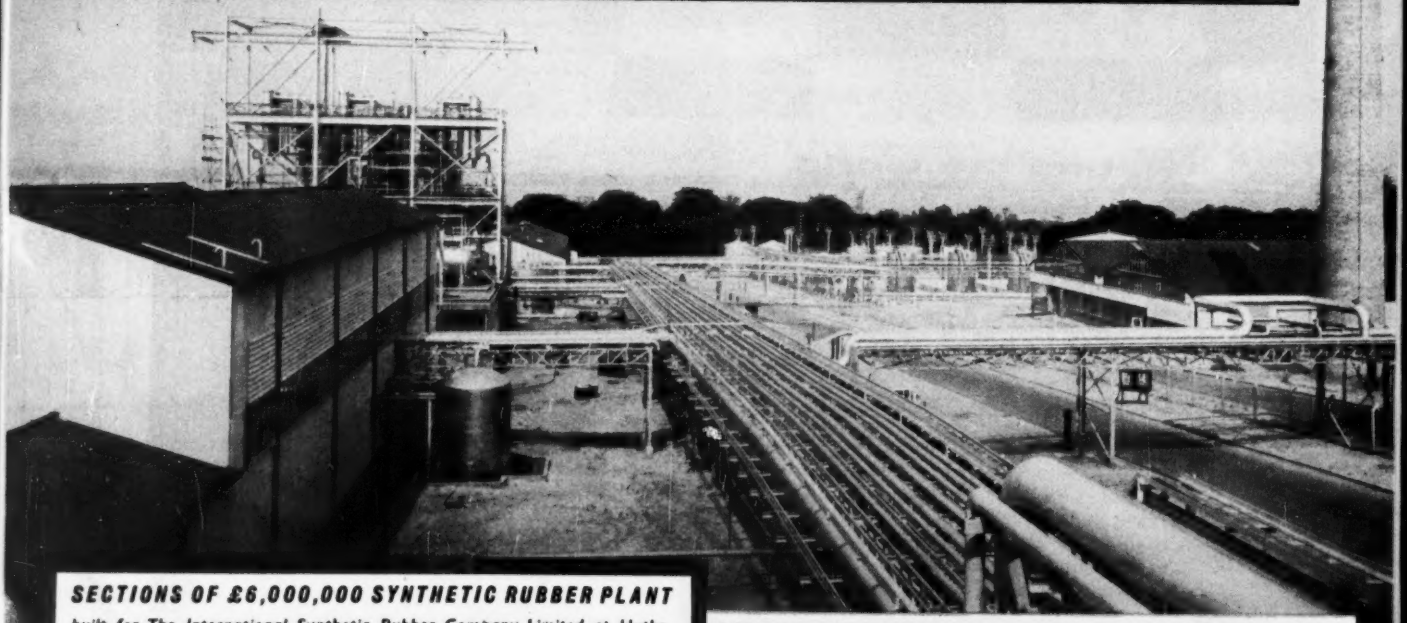

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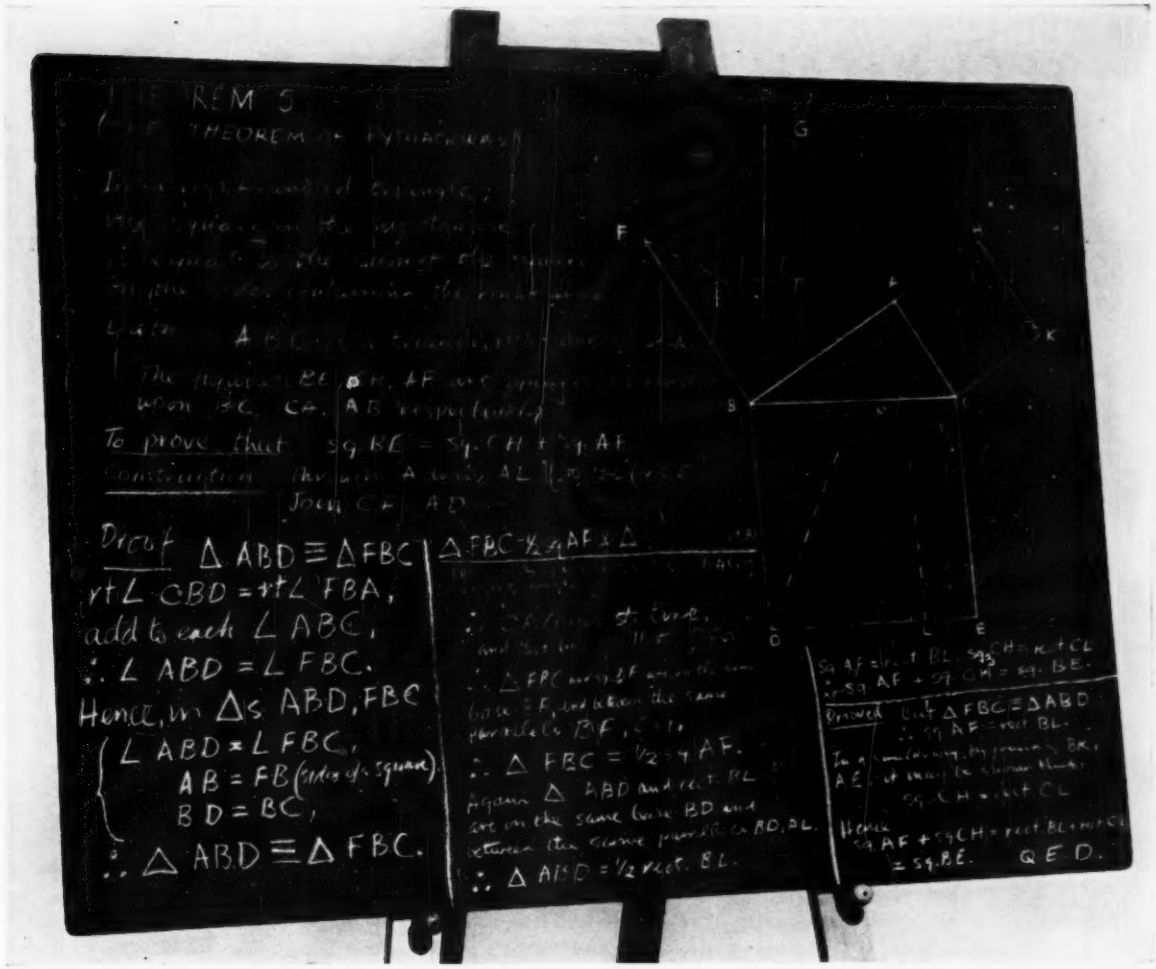

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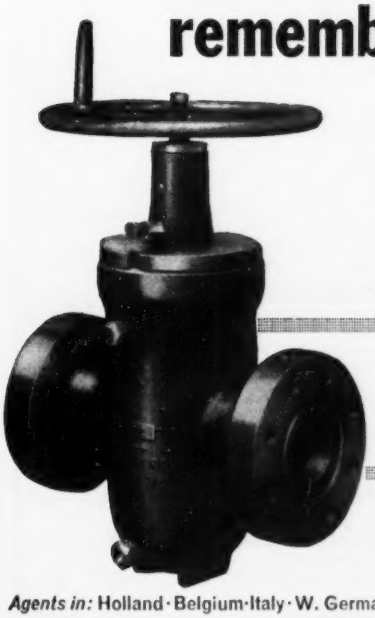

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WHY ALKYLATE IS THE KEY TO CURRENT GASOLINE BLENDING

OF THE FIVE typical high-quality blends which go into premium gasoline, alkylate is by far the best performer.

The reason is quite apparent in the table: Alkylate, though it can't claim the top research octane rating, does much better by the motor-octane method and, most important, excels in actual road performance.

The current controversy over methods of measuring octane ratings arises from the fact that, as the new cars become more demanding, the research octane rating becomes less indicative of actual fuel performance.

The old motor method, on the other hand, more closely matches actual driving performance, or road ratings.

In the past, top billing has gone to the research rating of gasoline. Even today, as it approaches or passes the magic 100 mark, research is getting a big play in advertising.

But the payoff is road performance. As requirements rise, today's cars are beginning to rate fuels more nearly as they are evaluated in the laboratory by the motor method. Both yardsticks are still important, but their relation to each other, called sensitivity, is something the industry is watching more closely.

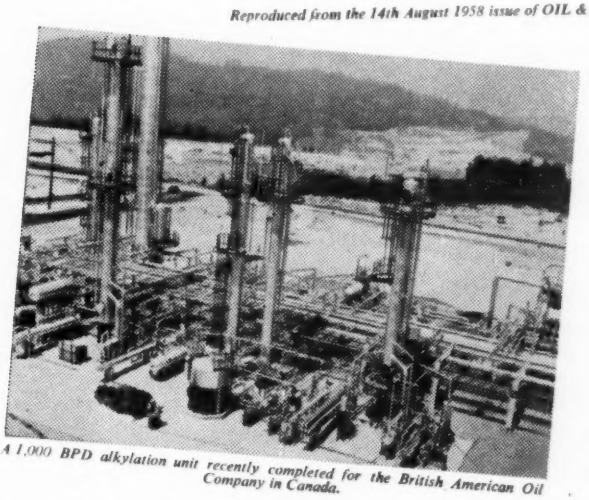
	Research octane (RON)	Motor octane (MON)	Sensitivity (RON minus MON)	Road octane (Uniontown)
Alkylate	103.0	104.5	— 1.5	107.5
Reformate extract	103.7	94.0	9.7	103.5
C_7 plus reformate	103.0	93.5	9.5	102.5
C_5 plus reformate	100.0	91.7	8.3	100.0
Catalytic cracked	99.0	87.5	11.5	98.0

Shown here are the antiknock values of five typical high-quality leaded blends. Note the more direct correlation of road with motor octane.

Note, too, that neither the research nor the motor method gives the refiner a direct fix on his ultimate goal—how the fuel is actually judged by the car on the road. The industry is dissatisfied with both laboratory methods on this count. But it must live with them until something better is developed.

Of all available stocks today, alkylate is the standout. Moreover, alkylate shows better road performance when blended with aromatics than with cat gasoline. Polymer gasoline ranks generally higher than cat cracked by the research method. But both motor and road tests downgrade this olefin to the point where it is now going out of the picture as a premium blending stock.

Reproduced from the 14th August 1958 issue of OIL & GAS JOURNAL an authoratitive U.S. petroleum publication.



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